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Original Paper

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Polymer-Laid Nonwovens From Poly (Lactide) Resin

Abstract

A poly (lactide) [PLA] thermoplastic polymer which is produced by polymerizing lactic acid (lactic acid is a fermentation product of corn dextrose) has been shown to be biodegradable by the manufacturer and was successfully melt blown on the 6-inch pilot line at TANDEC. A uniform melt blown web with good strength and hand was produced. Furthermore PLA was spunbond processed on the Reicofil 1-meter wide line on an exploratory basis at TANDEC and that also had good hand and mechanical properties. PLA exhibited acceptable processability in both melt blowing and spunbonding. The webs were characterized for fiber diameter, air permeability, filtration efficiency, tensile properties, and bursting strength. The melt blown PLA samples were comparable to conventional polypropylene webs in most properties including average fiber diameter. PLA webs had notably lower breaking elongation compared to typical PP webs. These lower than normal breaking elongations result in a very brittle structure. In terms of fiber diameter spunbond PLA web compared well to conventional PP spun bonded web and was lower in tensile breaking load and had much lower breaking elongation. This trend was the same as with melt blown PLA, making spunbonded webs very brittle. The shelf life of PLA is considerably less than PP and is affected to a significant degree by high temperature and humidity.

Introduction

With a steady increase in growth of nonwovens in both commercial and domestic sectors, their disposability is taking a more important role than ever before. The fast decline in landfill availability and growing concerns of incinerator emissions, the nonwovens industry as a whole is spending its resources on finding polymers and fibers which are biodegradable under composting or land filling conditions in a reasonably short period of time. With this in mind, research began at Textiles and Nonwovens Development Center (TANDEC) to develop nonwoven fabrics from inherently biodegradable polymers. The polymer chosen for this study, poly (lactide) is novel to the area of nonwovens and may hold certain unique characteristics compared to conventional thermoplastic resins used in melt blowing and spunbonding.

Poly (lactide) is a polymer produced by polymerizing lactic acid based on a patented process by Cargill[1] and is inherently biodegradable[2]. Figure 1 shows the schematic of Cargill PLA process. Lactic acid is obtained through fermentation of dextrose (a corn product) by same bacteria as in yogurt[3]. Lactic acid is optically active and is dimerized to produce a lactide which is also optically active (Meso-lactide, D-lactide, and L-lactide). The dimer is then ring opened to produce PLA. According to the manufacturer, properties of PLA such as degradation rates, strength, toughness, and crystallinity can be varied by changing optical composition of the dimer[3]. PLA appears to crystallize under spunbonding conditions but not much during melt blowing[3]. Since the glass transition temperature of PLA is ~60°C the material displays good dimensional stability even at low crystalline levels. PLA melts at 140-1[illegible]°C (comparable to PP) depending on the grade of the resin. PLA offers good resistance to solvents and has a shelf life of about one year. High temperatures and humidities such as those present in tropical climates are known to significantly reduce the shelf life of PLA[8]. Cargill's studies indicate that there is no significant deterioration in the physical properties of PLA after seven times reground[8].

Objectives

The primary objective of this research was to determine the suitability of PLA resin for melt blowing and spunbonding purposes. Additional objectives were to determine the processing

Cargill PLA Process

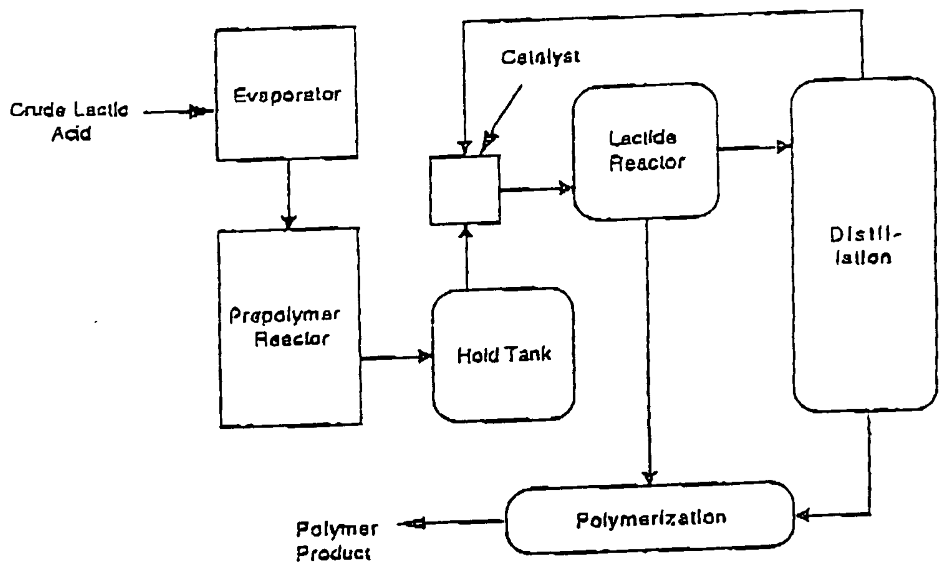

Figure 1. Schematic of Cargill's Poly (Lactide) Process[1]

performance during melt blowing and spunbonding and to characterize the webs produced in terms of fiber diameters and physical properties. Both melt blown and spunbond PLA webs were compared to normal PP melt blown and spunbond webs for fiber diameter and typical properties.

Background

Research in melt blowing of biodegradable resins dates back 1988 when L. C. Wadsworth obtained polyhydroxybutyrate (PHB) - polyhydroxyvalerate (PHV) polyester resin ("Biopol") from ICI Americas, Wilmington, DE. In 1991, PHB-PHV was successfully melt blown in 100% form, and also in blends with polypropylene and linear-low-density polyethylene[4]. Furthermore melt blown substrates made of 100% PHB-PHV and blends were laminated with carded cotton webs to produce thermally point bonded laminates that were found to be "inherently biodegradable"[4]. During the same time period of the TANDEC study, a US Patent was assigned to Shell Oil Company[5] for an invention relating to melt processing of blends of PP, PHB-PHV, and metal stearates. Other specialty biodegradable polymers such as polyvinyl alcohol and cellulose acetate have been melt blown at TANDEC[6] and promising results were obtained. It should be emphasized that there is no published literature documenting that melt blown and spunbond fabrics have here-to-fore been produced with PLA. It is also interesting to note that PLA resin is comparable in cost, to regular PP resins. The University of Tennessee Research Corporation has applied for US and foreign patents embodying concepts such as cotton-core laminates with a range of nonwoven outer layers as invented by L. C. Wadsworth, K. E. Duckett, and V. Balasubramanian.

Experimental

Processing - Melt Blowing

The polymer chosen for this study was PLA produced on a pilot scale by Cargill, Inc. The PLA thermoplastic resin was processed on a 0.15 m (6 inch wide) pilot melt blowing line equipped with a single screw extruder (25.4 mm screw diameter, 30/1 L/D). The nosetip has 794 holes/m (20 holes/inch). The air slot extends 0.0254m (1 inch) at each end of the orifices for a total air slot width of 0.20 m (8 inch). The nosetip has an orifice diameter of 0.508 mm (0.020 inch) and L/D ratio of 15/1. The air gap and nosetip setback were maintained constant at 2.54 and 1.63 mm (0.1 and 0.064 inch) respectively for the entire duration of the study. Table I shows the processing conditions employed during melt blowing. Since PLA resin was factory supplied in air tight containers there was no need for drying. If the resin had been supplied undried on-site drying must be done to a level of 100 ppm. The extruder hopper was covered and the resin was kept under a blanket of argon to prevent absorption of moisture. Sufficient quantities of webs were produced to facilitate detailed characterization. The basis weight was maintained at 34 g/m^2 (1.0 oz/yd^2).

Processing - Spunbonding

The PLA thermoplastic resin was processed on a 1.0 m (40 inch wide) Reicofil spunbonding line equipped with a single screw extruder. The spunbonding die has rows of orifices 0.4

TABLE I
Melt Blown Processing Conditions (PLA) for 6-inch Pilot Line

Sample No.	Orifice Dia., in./ L/D Ratio	Air Gap/ Setback, in.	Polymer Throughput, g/h/m	Basis Wt., oz/yd^2	Die Temp., °F	Air Temp., °F	Air Rate, std. ft^3/min/in.	DCD, in.
1	0.020/15/1	0.1/0.064	0.4	1.0	380	446	15.0	10
2	0.020/15/1	0.1/0.064	0.4	1.0	395	446	15.0	10
3	0.020/15/1	0.1/0.064	0.4	1.0	395	446	18.6	10
4	0.020/15/1	0.1/0.064	0.4	1.0	395	446	18.6	6
5	0.020/15/1	0.1/0.064	0.4	1.0	395	446	18.6	14
6	0.020/15/1	0.1/0.064	0.4	1.0	395	460	25.0	10
7	0.020/15/1	0.1/0.064	0.4	1.0	395	460	25.0	14
8	0.020/15/1	0.1/0.064	0.4	1.0	395	458	20.8	10

µm in diameter. The basis weight of spunbond webs was maintained at 60 g/m^2 (1.76 oz/yd^2). Table II shows the processing conditions used in spunbonding of PLA.

Characterization

Tests were performed on melt blown and spunbond samples of PLA to determine the average fiber diameter, variability of fiber diameter, air permeability, bursting strength, and tensile properties. Furthermore, melt blown PLA samples were characterized for NaCl aerosol filtration efficiency.

Fiber diameters of melt blown webs were measured from scanning electron micrographs of web samples obtained at a sufficient magnification to facilitate easy measurement. The fiber diameter was determined by drawing two opposing diagonal lines on a scanning electron micrograph and measuring all the fibers crossing the lines, making sure that each fiber was measured only once. For each sample a total of 75-100 individual measurements were made. The average fiber diameter was calculated and reported as an average of these individual measurements.

Fiber diameter of spunbond PLA webs was determined using a MTI CCD72S video camera fitted on a Olympus CH optical microscope. The image was captured on a Apple Macintosh IIci computer and the measurements were made using the "Image" software from National Institutes of Health (NIH).

Other properties such as, breaking load and elongation, bursting strength, air permeability, and sodium chloride aerosol filtration efficiency were determined according to standard test procedures listed in Table III.

TABLE II
Spunbond Processing Conditions (PLA) for 1-m Reicofil Line

Extruder Profile, °F	327-356
Die Temperature, °F	374
Polymer Throughput Rate, g/hole/min	0.13
Basis Weight, oz/yd^2	1.76
Calender Temperature, °F	Top=96; Bottom=100.7
Calender Pressure, PLI	254
Cooling Air Temperature, °F	46
Cooling Air Speed, RPM	805
Quench Chamber Pressure, Pa	0

Results and Discussion

Processing Observations

General. Poly (lactide) resin was successfully melt blown and spunbond on the 0.15 m (6 inch wide) pilot melt blowing line and 1 meter Reicofil line respectively. In both processes PLA displayed good processability and produced webs with a soft to moderate hand under the chosen processing conditions. The extruder and die temperature profiles were selected to ensure minimum thermal degradation of resins. The manufacturers' recommendations (7) on resin degradability were used as a guideline in choosing the processing temperatures.

Melt Blowing. The die temperature was maintained at 395°F (except in the case of sample #1, where it was 385°F) and the extruder was set in an ascending profile (360-380°F). The primary air temperature was kept at 446-460°F, similar range of normal polypropylene (PP). It is interesting to note that PLA could withstand an air rate as high as 25 std. ft^3/min/inch at a polymer throughput rate as low as 0.4 g/hole/min. The die-to-collector distance (DCD) was found to be critical. A closer DCD such as 6 inches gave a cohesive web with well balanced properties. The melt pressure for a polymer throughput of 0.4 g/hole/min was 110 psi which was in the similar range of 400 melt flow rate PP (typically about 200 at 560°F for a polymer throughput of 0.8 g/hole/min with a 0.508 mm orifice diameter and 10/1 L/D).

Spunbonding. The die temperature was maintained at 373°F and the extruder was set in an ascending profile (327-356°F). The melt pressure for a polymer throughput of 0.13 g/hole/min was 540 psi. These die melt pressures are considerably higher compared to regular 35 MFR spunbonding PP resins. The calender pressure had to be lowered to prevent sticking and to improve the handle of spunbond webs. Also, the calender oil temperature could be only slightly higher than the ambient temperature (86°F) at 108°F. Such lower bonding temperatures compared to PP (270-290°F) may have been due to the lower crystallizability of PLA. Evidence to this effect could be found during thermal calendering, whereby PLA spunbond web underwent considerable shrinkage as it emerged out of the calender nip. Once the amorphous orientation

TABLE III

Procedures for Web Property Characterization

Property	Basis
Air Permeability (Frazier)	ASTM Standard D737-75
Bursting Strength (Diaphragm type)	ASTM Standard D3786-87
Breaking Load and Elongation	ASTM Standard D1117-80
Average Fiber Diameter-MB	Scanning Electron Micrograph
Average Fiber Diameter-SB	Optical Microscope

the spin line it was disturbed by hot calender rolls. The PLA resin had a tendency to become sticky and hard to peel off the rolls. Also the lower resin throughput rate was necessary because a boardy web was obtained at higher throughput rates. The circu... ances point in the direction of lower crystallization rates, whereby uncrystallized fibers in the web fuse together with like fibers and other surrounding fibers resulting in a boardy web when passed between the thermal calender rolls. Given more time and stress (at lower throughputs the stress level on the filaments will be higher for the same suction fan speed) PLA fibers appear to form a soft spunbond web, which may be due to increased crystallization, and hence reduced sticking and fusing during thermal calendering.

Characterization of Webs

Melt Blown. Poly lactide (PLA) produced generally soft and uniform webs under the chosen processing conditions. The fiber diameter and mechanical properties for sample webs are listed in Table IV. The average fiber diameter and its variability for PLA webs were in the range of 3.01 to 6.45 μm with a coefficient of variation (C.V) of 27.3-56.2%. These values are comparable to those of typical PP melt blown webs (typical melt blown PP webs have an average fiber diameter of 2-4 μm and a C.V.% of fiber diameter of 25-60%), although the high end is out of range of typical filter quality MB PP webs.

The Frazier air permeability values for PLA webs were in the range of 90-271 ft^3/ft^2/min. These values are comparatively much higher than conventional PP melt blown webs (typically 50-150 ft^3/ft^2/min for 34 g/m^2 webs). This was expected, since the density of PLA is higher than PP the length of fibers in a certain volume of the web, for the same basis weight is smaller in the case of PLA web. Also the larger fiber diameter for some PLA webs would have resulted in higher air permeability values. The sodium chloride aerosol filtration efficiency values for MB PLA webs ranged from 37.3 to 65.28%. These values are similar to those of typical uncharged PP MB webs (25-65%).

Table IV also lists the test results of mechanical properties such as, bursting strength, machine direction (MD) breaking load, and peak breaking elongation. Cross direction (CD) tensile properties were not determined because the webs were not wide enough. PLA webs were stiffer and the breaking load and peak elongation were in the range of 1.00-4.77 lb/inch and 2.5-5.1% respectively. The breaking loads compare well with typical PP webs, but were more brittle (typical 1 oz/yd^2 PP melt blown webs have breaking loads of 0.8-3.5 lb/inch and peak elongations of 10-30%). The nature of tensile break indicated that PLA MB webs failed through fiber rupture. Further research towards web optimization may help improve these low elongation values. Bursting strength values for webs from either resin were comparable to those of typical PP webs of similar basis weight. Bursting strength values ranged from 7.6 to 10.6

TABLE IV

Test Results of Cargill PLA Melt Blown* and Spunbond‡ Samples

	Melt Blown PLA									Spunbond PLA	
Property	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5	Sample No. 6	Sample No. 7	Sample No. 8	Typical PP MB Webs	Sample No. 1	Typical PP SB Webs
Air Perm., ft^3/ft^2/min	270.8	246.54	175.28	90.34	227.06	103.18	136.94	149.00	50-150	351.8	300-500
Burst. Str., psi	8.25	9.25	9.58	7.58	8.58	8.75	10.58	10.00	6-10	8.4	20-30
Filtration Eff., %	38.85	37.30	43.18	60.03	47.73	65.28	59.03	46.95	25-60	—	—
Pk. Load, lb/in. (MD)	2.10	2.15	2.30	4.77	1.00	3.26	1.50	2.80	0.8-3.5	3.88/2.91 (MD/CD)	5-15
Pk Elong., % (MD)	3.10	2.80	3.70	3.90	2.50	5.10	3.00	4.40	10-30	6.6/7.4 (MD/CD)	100-300
Av. Fiber Dia, μm	6.45	6.41	4.55	5.34	4.85	3.01	3.21	4.03	2-4	16.85	15-35
C.V.% Fiber Dia,	32.4	27.3	33.6	33.9	37.1	56.2	50.2	35.7	25-40	19.25	3-8

* All MB samples were 1 oz/yd^2 (34 g/m^2) basis weight; ‡The SB sample was 1.76 oz/yd^2 (60 g/m^2).

psi. In comparison typical PP melt blown webs have bursting strength values ranging from approx. 6 psi to 10 psi for a basis weight of 1 oz/yd^2 (34 g/m^2).

Spunbond. The fiber diameter and mechanical properties for the spunbond PLA web are listed in Table IV. The fiber diameter of PLA spunbond was 16.85 (similar to a fine fibered PP spunbond) but the C.V.% of fiber diameter was much higher. PLA spunbond had a coefficient of variation of approx. 20% compared to 3-8% for a typical 35 MFR spunbond PP web. The molecular weight distribution of 35 MFR PP is tailored to be narrow which plays a very important role in affecting the fiber diameter distribution.

Spunbond PLA gave an air permeability value of 352 ft^3/ft^2/min. which is comparable to a typical PP spunbond (300-500 ft^3/ft^2/min) of the same basis weight (in this case 60 g/m^2). The bursting strength of spunbond PLA was 8.4 psi. [illegible]s bursting strength value is much lower compared to that of a typical PP spunbond (20-30 psi). Tensile properties of PLA spunbond are much different than regular PP spunbond webs. The machine direction (MD) breaking load was 3.88 lb/inch for PLA compared to 5-15 lb/inch for a typical PP spunbond. Breaking elongation value for PLA was 6.6%, which is extremely lower than PP spunbond (100-300%). The cross direction breaking load and elongation followed the same trend as MD.

Summary and Conclusions

PLA resin was successfully melt blown on the 6-inch melt blown line and spunbond on the 1-meter Reicofil spunbonding line at TANDEC. The melt blown and spunbond trials indicate a promising future for this novel and unique resin. The quality of melt blown and spunbond webs from PLA may be improved through tailoring of resin and process optimization. The resin used in this exploratory study behaved satisfactorily from the process point of view, but additional process and resin optimization studies could possibly lead to the development of webs with even smaller fiber diameters and further improved mechanical properties.

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Acknowledgments

The authors are thankful to Exxon Chemical Company for providing the melt blowing and Reicofil spunbonding equipment to TANDEC. The contributions of Mr. Richard Meade, Mr. Larry Spires, Mr. Gary Wynn, and Mr. Jack Wyrick during melt blown and spunbond trial runs for this study are greatly appreciated. The authors also express their appreciation to Ms. Liza Benson and Mr. Scott Strawn for assistance with physical characterization of webs.